Supporting Information

Exsolution of Catalytically Active Iridium Nanoparticles from Strontium Titanate

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S1. Image Analysis and Calculations

Particle size distribution and particle density were analyzed using ImageJ software. In order to calculate the number of exsolved Ir atoms ($N_{Ir_{exsolved}}$), the particles size and surface distribution (NP µm^{-2}) were integrated in the following calculations, based on similar work described previously: [1,2]

$$N_{Ir_{exsolved}} = \frac{4\pi\rho_{Ir}N_A}{3A_{Ir}} \sum_i f_i(\frac{d_i}{2})^3$$

Where ρ_{Ir} is density of Ir, N_A is the Avogadro's number, A_{Ir} is the atomic weight of Ir, f_i the fraction of exsolved nanoparticles (per µm^{-2} of perovskite) with diameter d_i.
The average number of Ir atoms in a perovskite grain of length L, width W and depth d was then calculated assuming a parallelepiped grain shape:

$$N_{Ir_{grain}} = \frac{LWd}{a_p^3} x_{Ir}$$

where x_{Ir} is the nominal doping concentration (x=0.5%).
By calculating the average surface area of one grain, it is possible to convert $N_{Ir_{exsolved}}$ in the number of exsolved Ir atoms per grain, which allowed us to calculate the concentration % of Ir exsolved compared to our nominal doping concentration (exsolved Ir concentration %= ∼0.2).
The total number of exsolved Ir atoms analysed in the XPS spot probing area ($N_{Ir_{XPS}}$) was then calculated, and related to the total number of Ti atoms analysed in the probing volume of XPS spot ($N_{Ti_{XPS}}$), considering a probing depth of 10 nm:

$$N_{Ti_{XPS}} = \frac{400 \times 0.01}{a_p^3} x_{Ti}$$

By relating this number to the Ti nominal concentration and comparing it with $N_{Ir_{XPS}}$, it was then possible to calculate the expected Ir concentration (%) in the probing XPS

spot volume, which, for the sample reduced at the highest temperature, was calculated as ∼2%, in good agreement with the 1.6% measured by XPS.

S2. Supplementary Data

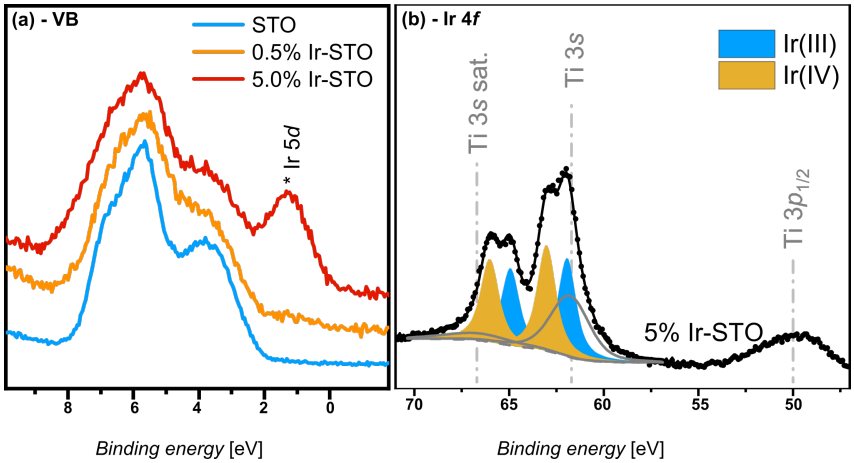

Figure S1: XPS analysis showing a) the valence band comparison for the undoped STO, 0.5% Ir-doped STO, and 5% Ir-doped STO; b) Ir 4*f* core level of 5% Ir-doped STO showing both Ir^{4+} and Ir^{3+} components.

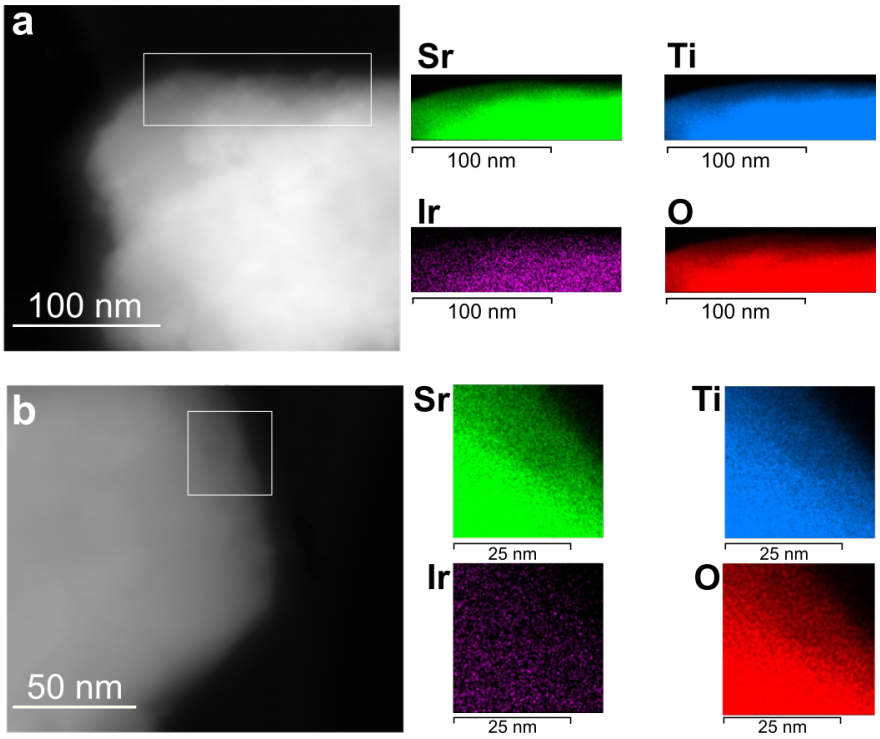

Figure S2: STEM-EDX elemental analysis carried out on the as-synthesised 0.5% Ir-doped STO. The areas analysed in the two different Ir-STO grains in a) and b) both show the homogeneous composition of the sample before reduction at high temperatures.

Table S1: XPS fit parameter for the Ir 4*f*, Ti 2*p*, Sr 3*d* and C 1*s* of the undoped STO, Ir-doped STO and Ir-doped STO reduced at 1100 °C and 1300 °C.

Core line	**BE (eV)**	**FWHM (eV)**	**SOS (eV)**	**Atomic %**
Undoped STO				
Sr $3d_{5/2}$ STO	132.65	0.9	1.76	39.97
Sr $3d_{5/2}$ $SrCO_3$	133.38	1.2	1.7	4.05
Ti $2p_{3/2}$	458.13	0.99	5.75	51.82
C 1*s* C=O	289.25	1.51	—	4.16
C 1*s* C-C	284.8	1.49	—	—
Ir doped STO	20^oC			
Ir $4f_{7/2}$ Ir(III)	61.79	1.2	3.00	0.41
Sr $3d_{5/2}$ STO	132.52	1.09	1.76	37.61
Sr $3d_{5/2}$ $SrCO_3$	133.5	1.19	1.75	12.10
Ti $2p_{3/2}$	458.05	1.27	5.71	49.88
C 1*s* C=O	289.25	1.51	—	14.76
C 1*s* C-C	284.8	1.45	—	—
Ir doped STO	1100^oC			
Ir $4f_{7/2}$ Ir(0)	59.95	1.19	3.10	0.62
Sr $3d_{5/2}$ STO	132.92	1.15	1.76	36.96
Sr $3d_{5/2}$ $SrCO_3$	133.82	1.25	1.73	14.11
Ti $2p_{3/2}$	458.4	1.29	5.78	39.96
C 1*s* C=O	289.66	1.41	—	8.34
C 1*s* C-C	284.8	1.41	—	—
Ir doped STO	1300^oC			
Ir $4f_{7/2}$ Ir(0)	59.80	1.00	3.07	0.65
Sr $3d_{5/2}$ STO	132.76	0.99	1.75	42.92
Sr $3d_{5/2}$ $SrCO_3$	133.74	1.09	1.7	7.76
Ti $2p_{3/2}$	458.17	1.02	5.73	39.38
C 1*s* C=O	289.64	1.38	—	9.30
C 1*s* C-C	284.8	1.25	—	—

Table S2: Sr_{SrCO_3} : $Sr_{lattice}$ before doping, after doping and after exsolution.

Samples	**Sr (surface)**	**Sr (bulk)**
Undoped STO	9.2 %	90.8 %
Ir-STO	24.3 %	75.7 %
Ir-STO, 900 °C	17.1%	82.9%
Ir-STO, 1100 °C	27.6 %	72.4 %
Ir-STO, 1300 °C	15.3 %	84.7 %

References

[1] C. Tang, K. Kousi, D. Neagu, J. Portolés, E. I. Papaioannou, I. S. Metcalfe, *Nanoscale*, **2019**, 11, 16935.
[2] D. Neagu, T.-S. Oh, D. N. Miller, H. Ménard, S. M. Bukhari, S. R. Gamble, R. J. Gorte, J. M. Vohs, J. T.S. Irvine, *Nature Commun.*, **2015**, 6, 8120.